

## Synthesis and Crystal Structures of Three New Hetero-binuclear Hg(II)-Cu(II) Schiff Base Complexes

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New hetero-binuclear Hg-Cu Schiff base complexes were prepared by reaction of 2,2'-[1,1'-(2,2-dimethylpropane-1,3-diyl)dinitrilo-diethyldyne]diphenolato}copper(II) ( $\text{CuL}^1$ ) and 6,6'-X-2,2'-[(2,2-dimethylpropane-1,3-diyl)bis(nitrimethanylylidene)]diphenolato copper(II) [(X = ethoxy ( $\text{CuL}^2$ ) and methoxy ( $\text{CuL}^3$ )], with  $\text{HgCl}_2$  to give  $[\text{Cu}(\text{L}^1)\text{HgCl}_2]$  (1),  $[\text{Cu}(\text{L}^2)\text{HgCl}_2]$  (2), and  $[\text{Cu}(\text{L}^3)\text{HgCl}_2]$  (3), respectively. In the precursor Cu(II) complexes ( $\text{CuL}^1$ - $\text{CuL}^3$ ), the coordinated phenolic oxygen atoms and those of the substituents at 3,3'-positions (in 2 and 3) on aromatic ring can act as additional site of coordination to  $\text{HgCl}_2$  as metallo-ligand to make heterobinuclear Cu-Hg complexes. The  $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^3$  Schiff base ligands were characterized by elemental analyses,  $^1\text{H}$  NMR and FT IR techniques. The related binuclear Cu-Hg complexes were characterized by elemental analyses and single-crystal X-ray diffraction. The main coordination sites for the  $\text{HgCl}_2$  unit are phenolic oxygen atoms and there are also short intramolecular  $\text{Hg}\cdots\text{O}$  (methoxy and ethoxy segments) contacts in 2 and 3. The crystal packing of 3 shows one-dimensional extended chains along the b-axis through pair of centro-symmetric  $\text{C-H}\cdots\text{Cl}$  interactions. The new complexes crystallize in *Pbca* (1), *P2<sub>1</sub>/n* (2), and *P2<sub>1</sub>/c* (3) space groups.

**Keywords:** Bimetallic complexes, Schiff base complexes, Mercury complexes

### INTRODUCTION

Since the Cu(II) ion is an essential element for all living beings, copper(II) complexes have been used in pharmacology. Among different ligands, Schiff base complexes are one of the most prevalent coordination ligands in coordination chemistry with ease of preparation and structural variations [1]. Metal complexes of Schiff base ligands were studied extensively, and Cu(II) complexes play a major role in both synthetic and structural research [2-3]. Usually, the oxygen atoms in (N,N,O,O) Schiff base complexes serve as donor atoms further coordinated to second metal ions so called metallo-ligands for formation of bimetallic complexes. Such interaction can be also realized in the presence of additional donor groups at 3,3'-positions of the benzene ring [4-6].

Mercury is also one of the most toxic heavy elements for animals and humans because secretion of mercury from the human body is very difficult. On the other hand, mercury compounds have interesting crystal structures [7-9] and mercury halides tend to dimerize forming planar  $\text{HgX}\cdots\text{XHg}$  (X = halides), coordination rings. For this reason, copper and mercury complexes are important in bioinorganic chemistry and the complexes which have both ions are very interesting from both toxicological and crystallographic points of view [10-12]. In this work, we describe how the (O,O) donor atoms of complex  $[\text{Cu}(\text{L}^1)]$  and  $\text{O}_4$ -cavity in complexes  $[\text{Cu}(\text{L}^2)]$ , and  $[\text{Cu}(\text{L}^3)]$  as metalloligand species bind to  $\text{HgCl}_2$  to form hetero-bimetallic complexes.

### EXPERIMENTAL

#### Materials and Methods

Reagents used for synthesis of compounds, were obtained from Merck and used as received. The solvents

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were dried before use with the appropriate drying reagents. Infrared spectra were recorded using KBr disks on a FT-IR Pertige21 spectrophotometer. Elemental analyses were performed on a Leco, CHNS-932 analyzer.  $^1\text{H}$  NMR spectra were measured on a 500 MHz BRUKER DRX-500 AVANCE spectrometer.

### Preparation of Ligands ( $\text{H}_2\text{L}^1$ , $\text{H}_2\text{L}^2$ and $\text{H}_2\text{L}^3$ )

**$\text{L}^1$ .** 2'-Hydroxyacetophenone (1.36 g, 10 mmol) was added to an ethanol solution (50 ml) of 2,2-dimethylpropanediamine (0.51 g, 5 mmol) and the mixture was refluxed for 3 h. The yellow precipitates of  $\text{H}_2\text{L}^1$  were collected by filtration, washed with ethanol and then dried *in vacuo* at room temperature. Yield: 78%. Anal. Calcd. for  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$ : C, 74.52; H, 7.74; N, 8.28%. Found: C, 74.63; H, 7.81; N, 8.19%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3039,  $\nu$  C-H (aliphatic): 2981, 2960,  $\nu$  C=N: 1614,  $\nu$  C=C and C-N: 1579, 1508, 1448, 1388,  $\nu$  C-O: 1238.  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 16.58 (broad, s, 2H, O-H), 7.52-7.54 (dd, 2H,  $J = 8.0, 1.2$ , H(6,6')), 7.28-7.33 (dt, 2H,  $J = 8.0, 1.2$ , H(5,5')), 7.93-6.95 (dd, 2H,  $J = 8.0, 1.2$ , H(3,3')), 6.77-6.81 (dt, 2H,  $J = 8.0, 1.2$ , H(4,4')), 3.55 (s, 4H,  $\text{CH}_2\text{-N}$ ), 2.35 (s, 6H,  $\text{CH}_3\text{-C=N}$ ), 1.24 (s, 6H,  $\text{CH}_3\text{-C}$ ).

**$\text{L}^2$ .** 2-Hydroxy-3-ethoxybenzaldehyde (1.66 g, 10 mmol) was added to an ethanol solution (50 ml) of 2,2-dimethylpropanediamine (0.51 g, 5 mmol) and the mixture was refluxed for 1 h. The yellow precipitates of  $\text{H}_2\text{L}^2$  were collected by filtration, washed with ethanol and then dried *in vacuo* at room temperature. Yield: 89%. Anal. Calcd. for  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_4$ : C, 69.32; H, 7.59; N, 7.03%. Found: C, 69.43; H, 7.63; N, 6.93%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3043,  $\nu$  C-H (aliphatic): 2983, 2879,  $\nu$  C=N: 1637,  $\nu$  C=C and C-N: 1579, 1495, 1458, 1386,  $\nu$  C-O: 1246.  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 14.05 (broad, s, 2H, O-H), 8.36 (s, 2H, H-C=N), 6.95-6.97 (dd, 2H,  $J = 8.0, 1.2$ , H(6,6')), 6.90-6.92 (dd, 2H,  $J = 8.0, 1.2$ , H(4,4')), 6.83 (t, 2H,  $J = 8.0$ , H(5,5')), 4.16 (q, 2H,  $J = 7.0$ ,  $-\text{CH}_2\text{-O}$ ), 3.53 (s, 4H,  $-\text{CH}_2\text{-N}$ ), 1.53 (t, 6H,  $J = 7.0$ ,  $\text{CH}_3\text{-CH}_2\text{O}$ ), 1.13 (s, 6H,  $\text{CH}_3\text{-C}$ ).

**$\text{L}^3$ .** 2-Hydroxy-3-methoxybenzaldehyde (1.52 g, 10 mmol) was added to an ethanol solution (50 ml) of 2,2-dimethylpropanediamine (0.51 g, 5 mmol) and the mixture was refluxed for 1 h. The yellow precipitates of  $\text{H}_2\text{L}^3$  were collected by filtration, washed with ethanol and then dried *in vacuo* at room temperature. Yield: 81%. Anal. Calcd. for

$\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4$ : C, 68.09; H, 7.07; N, 7.56%. Found: C, 68.21; H, 7.11; N, 7.48%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3055,  $\nu$  C-H (aliphatic): 2926, 2850,  $\nu$  C=N: 1627,  $\nu$  C=C and C-N: 1564, 1510, 1475, 1340,  $\nu$  C-O: 1253.  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (ppm)]: 14.12 (broad, s, 2H, O-H), 8.20 (s, 2H, H-C=N), 7.14-7.16 (dd, 2H,  $J = 8.5, 2.2$ , H(6,6')), 6.45-6.47 (dd, 2H,  $J = 8.5, 2.2$ , H(4,4')), 6.43 (t, 2H,  $J = 8.5$ , H(5,5')), 3.86 (s, 6H,  $-\text{OCH}_3$ ), 3.46 (s, 4H,  $\text{CH}_2\text{-N}$ ), 1.10 (s, 6H,  $\text{CH}_3\text{-C}$ ).

### Preparation of Mononuclear CuL Complexes

**Synthesis of  $\text{CuL}^1$ .** {2,2'-[1,1'-(2,2-Dimethylpropane-1,3-diylidinitrilo)-diethyldyne]diphenolato}  $\text{L}^1$  (1.120 g, 4 mmol) was dissolved in methanol (60 ml). This solution was heated to boiling and a solution of  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  (0.682 g, 4 mmol) in hot water (30 ml) was added. The resulting mixture was left to stand for 2 h. The green copper(II) complex which formed was filtered off and dried at 383 K for 3 h. The same procedure was used for preparation of  $\text{CuL}^2$  and  $\text{CuL}^3$  using  $\text{L}^2$  and  $\text{L}^3$  as ligand, respectively.

**$\text{CuL}^1$ .** Yield: 57%. Anal. Calcd. for  $\text{C}_{21}\text{H}_{24}\text{CuN}_2\text{O}_2$ : C, 63.06; H, 6.05; N, 7.00%. Found: C, 62.91; H, 6.01; N, 7.07%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3055,  $\nu$  C-H (aliphatic): 2962, 2810,  $\nu$  C=N: 1610,  $\nu$  C=C and C-N: 1585, 1537, 1442, 1373,  $\nu$  C-O: 1325.

**$\text{CuL}^2$ .** Yield: 73%. Anal. Calcd. for  $\text{C}_{23}\text{H}_{28}\text{CuN}_2\text{O}_4$ : C, 60.05; H, 6.13; N, 6.09%. Found: C, 60.23; H, 6.18; N, 5.92%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3053,  $\nu$  C-H (aliphatic): 2922, 2872,  $\nu$  C=N: 1622,  $\nu$  C=C and C-N: 1566, 1546, 1444, 1352,  $\nu$  C-O: 1319.

**$\text{CuL}^3$ .** Yield: 68%. Anal. Calcd. for  $\text{C}_{21}\text{H}_{24}\text{CuN}_2\text{O}_4$ : C, 58.39; H, 5.60; N, 6.48%. Found: C, 58.21; H, 5.68; N, 6.57%. IR (KBr pellet  $\text{cm}^{-1}$ ):  $\nu$  C-H (aromatic): 3049,  $\nu$  C-H (aliphatic): 2959, 2866,  $\nu$  C=N: 1618,  $\nu$  C=C and C-N: 1543, 1529, 1462, 1388,  $\nu$  C-O: 1321.

**Synthesis of binuclear Cu-Hg complexes Complex 1: [ $\text{CuL}^1\text{HgCl}_2$ ].** The prepared  $\text{CuL}^1$  complex (0.344 g, 1 mmol) was dissolved in hot MeOH (50 ml). A solution of  $\text{HgCl}_2$  (0.271 g, 1 mmol) in hot MeOH (20 ml) was added rapidly to this solution. The green crystals suitable for X-ray diffraction analysis which formed after 24 h were filtered off and dried in air. Anal. Calcd. for 1(%): C, 37.56; H, 3.60; N, 4.17. Found: C, 37.51; H, 3.58; N, 4.19.

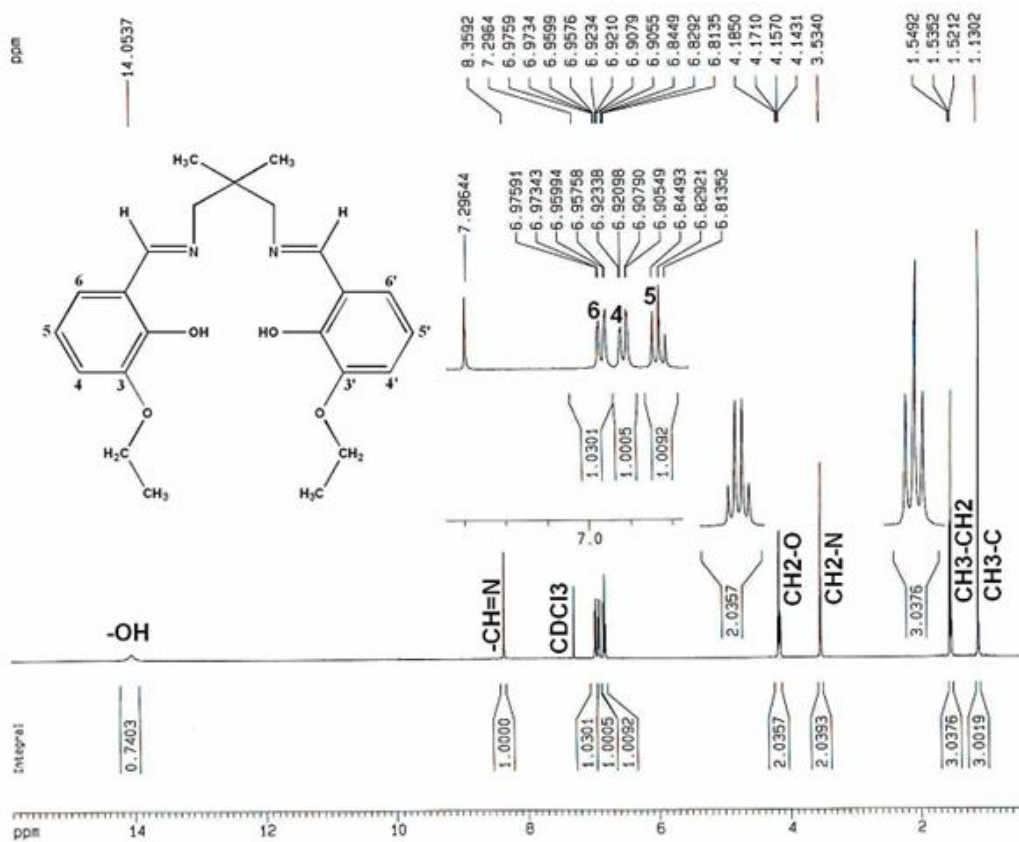
**Synthesis of 2 & 3: [CuL<sup>2</sup>HgCl<sub>2</sub>] and [CuL<sup>3</sup>HgCl<sub>2</sub>].**

Complex 2 and 3 were synthesized by the same procedure of complex 1 using CuL<sup>2</sup> and CuL<sup>3</sup> instead of CuL<sup>1</sup> complex. The green crystals were filtered off and dried in air. Anal. Calcd. for 2(%): C, 38.61; H, 4.19; N, 3.75. Found: C, 38.20; H, 4.14; N, 3.89. 3(%): C, 35.85; H, 3.44; N, 3.98. Found: C, 35.81; H, 3.45; N, 3.41.

**Crystal Structure Determination**

For obtaining the suitable crystals for X-ray crystallography, the complexes were dissolved in methanol and a crystals were grown by slow evaporation of the solvent. Single crystal X-ray data for complexes 1, 2 and 3 were collected at 296(1) K on STOE IPDS II diffractometer (Mo K $\alpha$  = 0.71073 Å). The cell parameters were retrieved using X-AREA [13] software and refined using X-AREA

on all observed reflections. Data reduction and correction for *Lp* (Lorentz-polarization) and decay were performed using X-AREA software. Absorption corrections were applied using MULABS [14] routine in PLATON [15]. All structures were solved by direct methods and refined by full-matrix least squares on F<sup>2</sup> for all data using SHELXTL [16] software. All calculations were performed by PLATON. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined with a riding model approximation with their parameters constrained to the parent atom with  $U_{iso}$  (H) = 1.2 or 1.5  $U_{eq}$  (C). The -CH<sub>3</sub> segment in one of the ethyl groups of complex 2 is disordered over two positions with a refined site occupancy of 0.54(8)/0.46(8). The single crystal of complex 2 was not optimal (low diffracting power) and due to the lack of low



**Fig. 1.** <sup>1</sup>H NMR spectrum of H<sub>2</sub>L<sup>2</sup>. The inset shows the expansion of the aromatic region and scheme of the ligand with numbering.

temperature device for data collection at low temperature it was not possible to get completeness more than 0.81% also because of the instability of the complex we covered the crystal with super glue so that the completeness scarified because of fast data collection.

## RESULTS AND DISCUSSION

The spectral data of the ligands are shown in the experimental section but the  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^2$  ligand (Fig. 1) is shown here in details. The  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^2$  shows a signal at  $\delta = 14.05$  ppm which is assigned to the proton of the phenolic group. Furthermore, the azomethine proton is observed as a singlet at  $\delta = 8.36$  ppm. The aromatic protons present at  $\delta = 6.81$ - $6.97$  ppm. The  $\text{H}_{(6)}$  signal is observed at  $\delta = 6.96$  ppm as doublet of doublet due to coupling with the  $\text{H}_{(5)}$  and  $\text{H}_{(4)}$ . The  $\text{H}_{(4)}$  is appeared at  $\delta = 6.91$  ppm as doublet of doublet due to its couplings with  $\text{H}_{(5)}$  and  $\text{H}_{(6)}$ . The  $\text{H}_{(5)}$  is observed at  $\delta = 6.83$  ppm as triplet due to coupling with the  $\text{H}_{(4)}$  and  $\text{H}_{(6)}$ . A quartet at  $\delta = 4.16$  ppm [ $^3J(\text{H,H}) = 7.0$  Hz] is assigned to the  $-\text{OCH}_2$  protons, coupled with the  $-\text{CH}_3$  protons, while a triplet at  $\delta = 1.53$  ppm [ $^3J(\text{H,H}) = 7.0$  Hz] is assigned to the  $-\text{CH}_3$  protons, coupled with the  $-\text{OCH}_2$  protons. The methylene protons ( $\text{CH}_2\text{-N}$ ) are observed at  $\delta = 3.53$  ppm and the methyl protons ( $\text{CH}_3\text{-C}$ ) are observed at  $\delta = 1.13$  ppm as singlet.

The information about the bond lengths, stretching

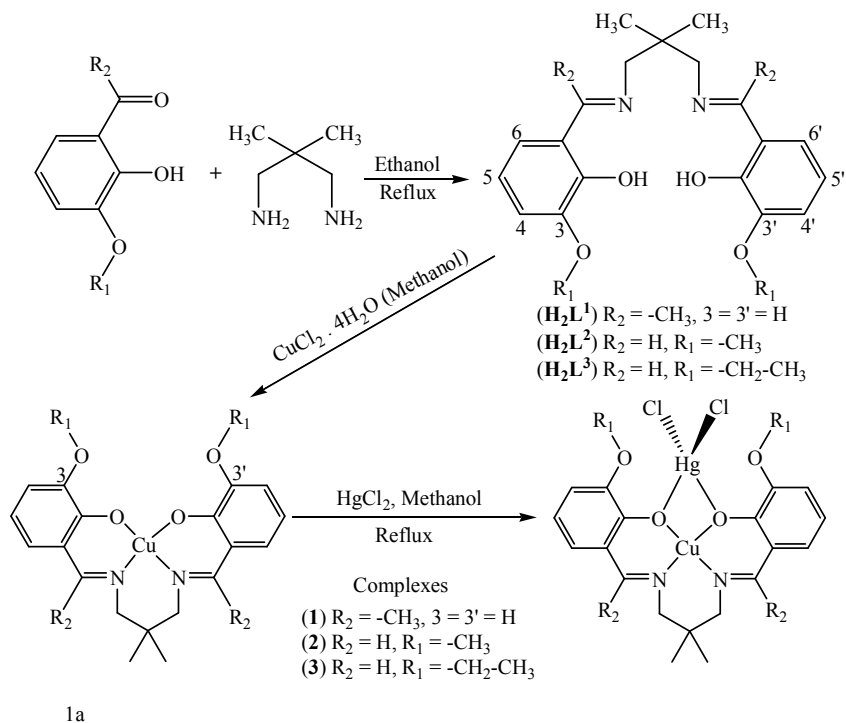
frequencies of the  $\text{C}=\text{N}$  and  $\text{C}-\text{O}$  bonds of the ligands and their mononuclear  $\text{Cu}(\text{II})$  complexes are summarized in Table 1. The strong bands around  $1614$ - $1637$   $\text{cm}^{-1}$  in the FT IR spectra of ligands are attributed to the azomethine stretching band which are red shifted to  $1610$ - $1622$   $\text{cm}^{-1}$  upon coordination to  $\text{Cu}(\text{II})$  ion. While the  $\text{C}-\text{O}$  stretching band of the ligands shift from  $1238$ - $1253$   $\text{cm}^{-1}$  to  $1319$ - $1325$   $\text{cm}^{-1}$  upon coordination to  $\text{Cu}(\text{II})$  ion. These observations are in accordance with the data obtained for the  $\text{C}=\text{N}$  and  $\text{C}-\text{O}$  bonds lengths by X-ray crystallography in which the  $\text{C}=\text{N}$  bond is weakened by coordination to  $\text{Cu}(\text{II})$ . In contrast, the  $\text{C}-\text{O}$  bond is strengthened upon coordination to  $\text{Cu}(\text{II})$  [17]. Furthermore, reaction of 2,2'-[1,1'-(2,2-dimethylpropane-1,3-diyl)dinitrilo]-diethyldyne]diphenolato} copper(II) ( $\text{CuL}^1$ ) and 6,6'-X-2,2'-[(2,2-dimethylpropane-1,3-diyl)bis(nitrilomethanylylidene)] diphenolato copper(II) [(X = ethoxy ( $\text{CuL}^2$ ) and methoxy ( $\text{CuL}^3$ )], with  $\text{HgCl}_2$  afforded the title compounds which can be formulated as [ $\text{CuL}^1(\text{HgCl}_2)$ ], [ $\text{CuL}^2(\text{HgCl}_2)$ ] and [ $\text{CuL}^3(\text{HgCl}_2)$ ] (Scheme 1a).

These new compounds were characterized by elemental analysis, and their structures have been unambiguously determined by single-crystal X-ray crystallography. The asymmetric unit of the complexes 1-3 is shown as ORTEP plot in Figs. 2-4, respectively. The crystal parameter and refinement data are summarized in Table 2.

The selected bond distances and lengths are shown in Table 3. The information of the intermolecular  $\text{C}-\text{H}\cdots\text{Cl}$

**Table 1.** Comparison of the Bond Lengths and Stretching Frequencies of  $\text{C}=\text{N}$  and  $\text{C}-\text{O}$  Bonds in the Ligands and the Related  $\text{CuL}$  Complexes

Compound	N=C (averaged) (Å)	$\nu$ C=N ( $\text{cm}^{-1}$ )	C1-O1 (averaged) (Å)	$\nu$ C-O ( $\text{cm}^{-1}$ )
$\text{H}_2\text{L}^1$	1.283	1614	1.344	1238
$\text{CuL}^1$	1.284	1610	1.307	1325
$\text{H}_2\text{L}^2$	1.278	1637	1.350	1246
$\text{CuL}^2$	1.291	1622	1.306	1319
$\text{H}_2\text{L}^3$	1.282	1628	1.351	1253
$\text{CuL}^3$	1.287	1618	1.314	1321



Scheme 1. Reaction pathways for synthesis of the ligands and their related Cu(II) and binuclear Cu-Hg complexes.

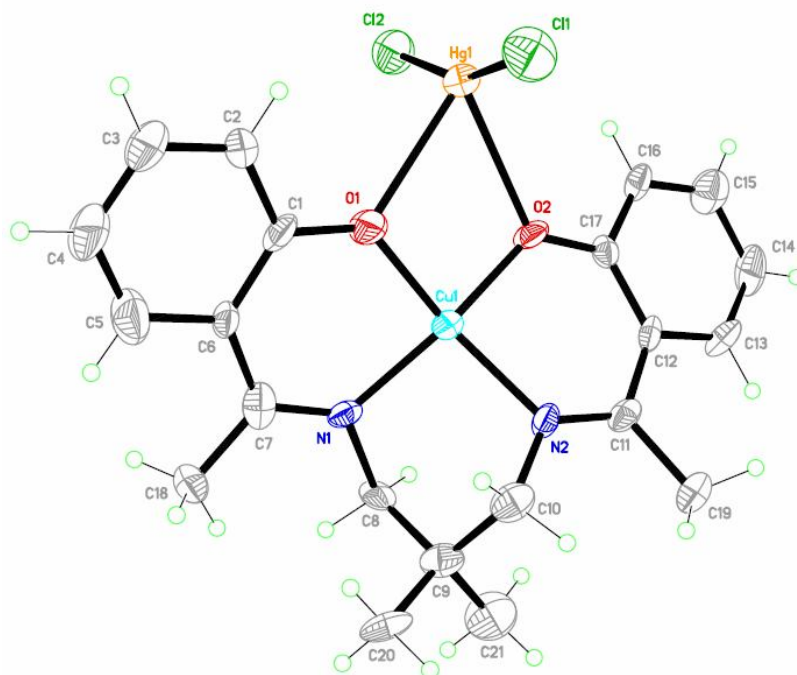
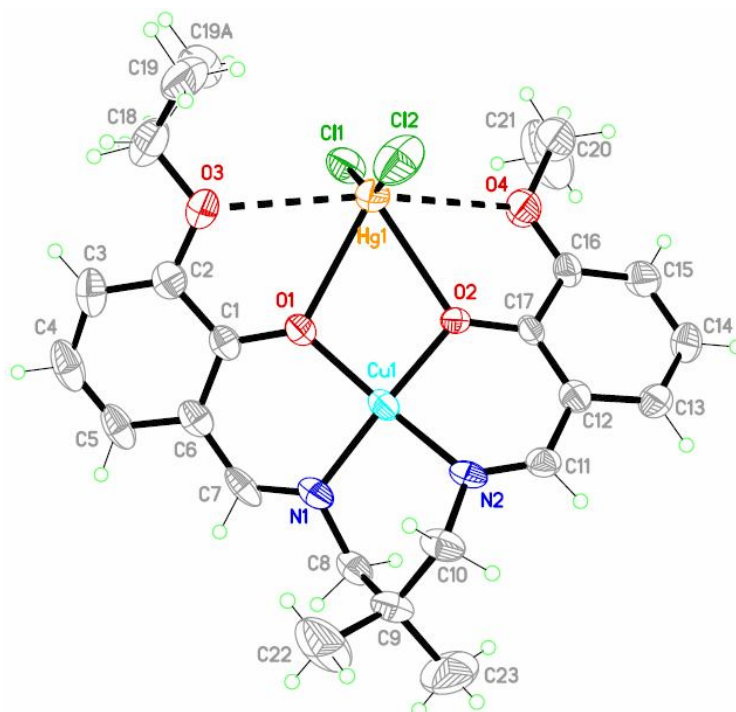
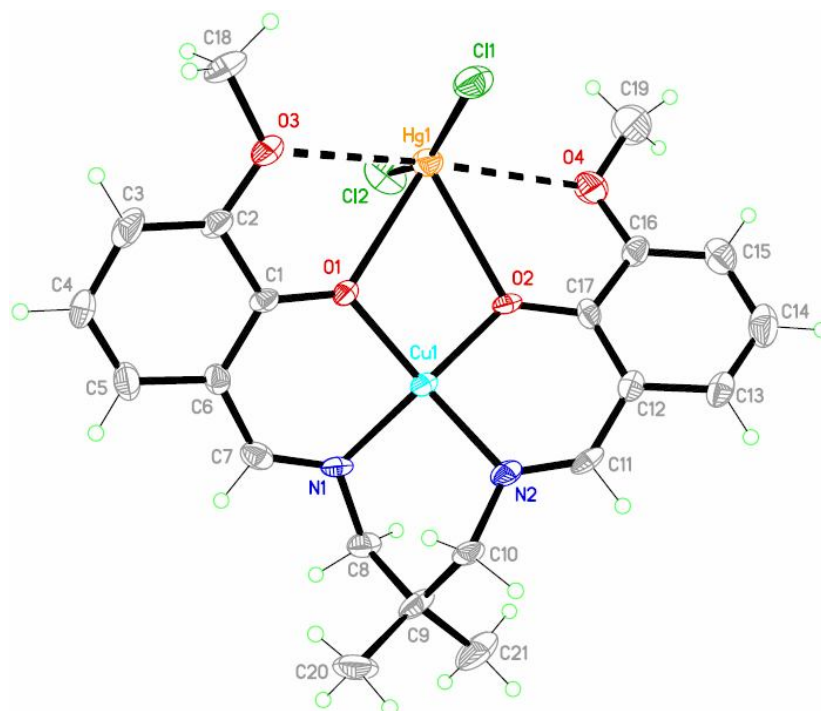


Fig. 2. The molecular structure of complex 1, showing 40% probability displacement ellipsoids and the atomic numbering.



**Fig. 3.** The molecular structure of complex 2, showing 40% probability displacement ellipsoids and the atomic numbering. The dashed line shows short intramolecular Hg $\cdots$ O contacts.



**Fig. 4.** The molecular structure of complex 3, showing 40% probability displacement ellipsoids and the atomic numbering. The dashed line shows short intramolecular Hg $\cdots$ O contacts.

**Table 2.** Crystal Data and Structure Refinement Parameters for Complexes 1-3

Empirical formula	C <sub>21</sub> H <sub>24</sub> Cl <sub>2</sub> CuHgN <sub>2</sub> O <sub>2</sub>	C <sub>23</sub> H <sub>28</sub> Cl <sub>2</sub> CuHgN <sub>2</sub> O <sub>4</sub>	C <sub>21</sub> H <sub>24</sub> Cl <sub>2</sub> CuHgN <sub>2</sub> O <sub>4</sub>
Formula mass	671.45	731.50	570.04
Crystal size (mm)	0.43 × 0.22 × 0.11	0.41 × 0.20 × 0.10	0.50 × 0.28 × 0.06
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>
$\theta_{max}$ (°)	25	25.49	25.50
<i>a</i> (Å)	15.348(3)	12.385(5)	11.911(2)
<i>b</i> (Å)	14.875(3)	12.237(5)	11.784(3)
<i>c</i> (Å)	19.722(4)	17.714(5)	17.0802(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	102.274(5)	117.815(13)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	4502.8(16)	2623.3(17)	2435.5(9)
<i>Z</i>	8	4	4
<i>D</i> <sub>calc</sub> (mg m <sup>-3</sup> )	1.981	1.852	1.918
$\mu$ (mm <sup>-1</sup> )	8.012	6.890	7.417
<i>F</i> (000)	2584	1420	1356
Index ranges	-16 ≤ <i>h</i> ≤ 18 -17 ≤ <i>k</i> ≤ 17 -23 ≤ <i>l</i> ≤ 20	-13 ≤ <i>h</i> ≤ 14 -14 ≤ <i>k</i> ≤ 13 -21 ≤ <i>l</i> ≤ 21	-10 ≤ <i>h</i> ≤ 14 -12 ≤ <i>k</i> ≤ 14 -23 ≤ <i>l</i> ≤ 23
No. of measured Reflections	14220 3933/0.1297	8993 3948/0.0505	10378 4227/0.0783
No. of independent Reflections/ <i>R</i> <sub>int</sub>	2322	2591	2551
No. of observed Reflections	264	311	282
with <i>I</i> > 2σ( <i>I</i> )	0.933	1.009	0.937
No. of parameters	0.0547	0.0464	0.0518
Goodness-of-fit (GOF)	0.1029	0.0906	0.1001
<i>R</i> <sub>1</sub> (observed data)			
<i>wR</i> <sub>2</sub> (all data) <sup>a</sup>			

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$  for 1,  $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$  for 2,  $w = 1/[\sigma^2(F_o^2) + 0.0522P]^2 + 2.4507P]$  for 3, where  $P = (F_o^2 + 2F_c^2)/3$

**Table 3.** Selected Bond Distances (Å) and Angles (°) for Complexes 1-3

	Complex 1	Complex 2	Complex 3
Cu(1)-O(1)	1.869(8)	1.894(6)	1.901(7)
Cu(1)-O(2)	1.888(8)	1.902(6)	1.899(7)
Cu(1)-N(1)	1.962(10)	1.926(8)	1.913(9)
Cu(1)-N(2)	1.974(9)	1.941(8)	1.940(9)
C(7)-N(1)	1.301(14)	1.288(12)	1.291(13)
C(11)-N(2)	1.286(14)	1.276(10)	1.274(13)
Hg(1)-Cl(1)	2.310(4)	2.319(3)	2.304(3)
Hg(1)-Cl(2)	2.304(4)	2.323(3)	2.316(3)
Hg(1)···O(3)		2.893(7)	2.895(7)
Hg(1)···O(4)		2.912(9)	2.867(9)
N(1)-Cu(1)-N(2)	94.9(4)	92.4(1)	91.2(4)
O(1)-Cu(1)-O(2)	87.8(3)	87.9(2)	88.0(3)
N(1)-Cu(1)-O(2)	160.6(4)	160.2(3)	160.2(3)
N(2)-Cu(1)-O(1)	159.7(4)	160.8(3)	158.7(3)
Cl(1)-Hg(1)-Cl(2)	160.33(15)	152.62(12)	153.51(14)
O(3)···Hg(1)···O(4)		162.3(2)	165.0(3)

**Table 4.** Parameters of Intermolecular Interactions in Complexes 2-3

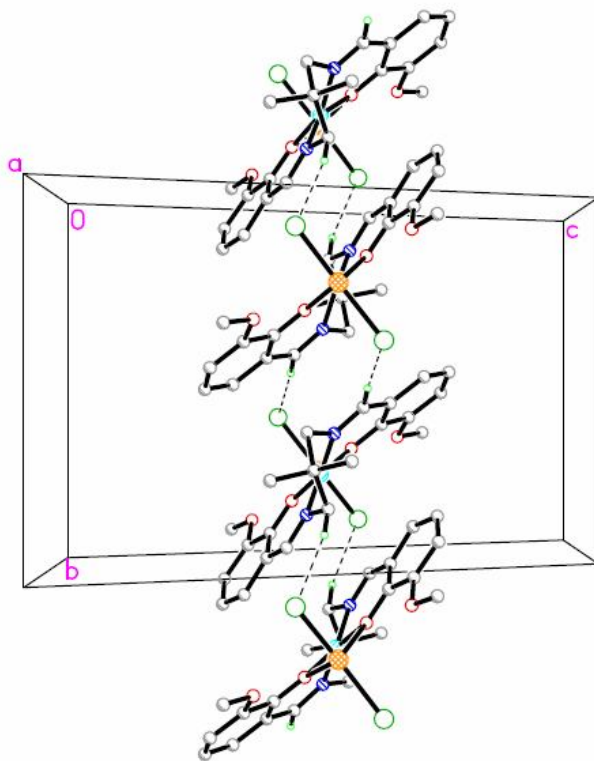
	D-H···A	H···A (Å)	D···A (Å)	D-H···A (°)
Complex 2	C8-H8B···Cl1 <sup>a</sup>	2.80	3.757(11)	169
	C11-H11A···Cl2 <sup>b</sup>	2.82	3.746(11)	173
Complex 3	C7-H7A···Cl2 <sup>c</sup>	2.79	3.709(13)	172
	C10-H10B···Cl1 <sup>d</sup>	2.71	3.667(12)	167

Symmetry codes: <sup>a</sup>1 - x, -y, 1 - z. <sup>b</sup>1 - x, 1 - y, 1 - z. <sup>c</sup>1 - x, -y, -2 - z. <sup>d</sup>1 - x, 1 - y, -2 - z.

interactions for complexes 2 and 3 are shown in Table 4. The crystal structures of the related starting mononuclear Cu(II) complexes, [CuL<sup>1</sup>, CuL<sup>2</sup> and CuL<sup>3</sup>], in this study were reported previously [18-20]. The bond lengths [21]

and angles in the binuclear Hg-Cu complexes are within the normal ranges and are comparable to the related mononuclear Cu(II) complexes. The Cu(II) centre has a distorted square-planar coordination involving two O and





**Fig. 5.** The crystal packing of complex 3, showing the one-dimensional extended chain along the *b*-axis.

two N atoms from the Schiff base ligands and, with Cu-O [1.869(8) and 1.926 (2) Å for 1; 1.894(6) and 1.902(6) for 2; 1.899(7) and 1.901(7) for 3] and Cu-N [1.962(10) and 1.974(9) Å for 1; 1.926(8) and 1.941(8) for 2; 1.913(9) and 1.940(9) Å for 3] which are comparable to the previously reported structures [10-12]. The dihedral angles between the coordination planes [O1-Cu1-N1 and O2-Cu1-N2] are 27.3(4)°, 26.7(3)° and 28.2(5)° in complexes 1, 2 and 3, respectively. The most significant geometric changes were observed in the coordination around the Hg(II) centre. Solid HgCl<sub>2</sub> was found to be linear, with Hg-Cl and Hg···Cl (neighbor) distances of 2.25 and 3.34 Å, respectively [22], but the Cl-Hg-Cl angles in 1-3 are 160.33(15)°, 152.62(12)° and 153.51(14)°, respectively, which show distorted tetrahedral geometries around Hg(II). In 2 and 3, the oxygen atoms of the 3,3'-methoxy and ethoxy substituents of the phenol segments show short contact interactions [Hg1···O3 = 2.893(7) & 2.895(7) Å for 1 and Hg1···O4 = 2.912(9) &

2.867(9) Å for 2] with the Hg(II) centre (dashed solid lines in Figs. 2 and 3) which are shorter than the sum of the van der Waals radii of these atoms (3.07 Å) [23]. There is no short Cu···Cl contact interactions in 1 and also the absence of these interactions are more pronounced in 2 and 3 because of the significant short Hg···O (3,3'-ring positions) contacts which prevent tilting of the HgCl<sub>2</sub> segment from the O1-Cu-O2 coordination plane. The crystal packing diagrams of complexes 2 and 3 shows interesting intermolecular C-H···Cl interactions (Table 4). These intermolecular interactions link neighboring molecules together, forming a one-dimensional extended chain along the *b*-axis in 2 (Fig. 5).

## SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data

Centre, CCDC Nos. 873110-873112 for complexes 1-3, respectively. Copies of this information may be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336-033; email: [deposit@ccdc.ac.uk](mailto:deposit@ccdc.ac.uk)).

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## REFERENCES

- [1] A.D. Granovski, A.L. Nivorozhkin, V.I. Minkin, *Coord. Chem. Rev.* 126 (1993) 1.
- [2] O. Atakol, C. Arici, M.N. Tahir, A. Kenar, D. Ulku, *Acta Cryst. C55* (1999) 1416.
- [3] P.J. Blower, *Transition Met. Chem.* 23 (1998) 109.
- [4] D. Cunningham, P. McArdle, Mitchell, N. Chonchubhair, M. O’Gara, F. Franceschi, C. Floriani, *Inorg. Chem.* 39 (2000) 1639.
- [5] D. Cunningham, J.F. Gallagher, T. Higgins, P. McArdle, D. Sheerin, *J. Chem. Soc., Chem. Commun.* (1991) 432.
- [6] S.D. Angelis, E. Solari, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Inorg. Chem.* 35 (1996) 5995.
- [7] D. Grdenic, *Rev. Chem. Soc.* 19 (1965) 303.
- [8] F.A. Cotton, G. Wilkinson, *Anorganische Chemie*, Weinheim, Interscience Publishers, 1967.
- [9] N.L. Holy, N.C. Baezinger, R.M. Flynn, D.C. Swendon, *J. Am. Chem. Soc.* 98 (1976) 7823.
- [10] I. Ercan, F. Ercan, C. Arici, O. Atakol, *Acta Cryst. C58* (2002) m137.
- [11] F.B. Kaynak, D. Ulku, O. Atakol, D. Durmu, *Acta Cryst. C55* (1999) 1784.
- [12] E.C. Constable, G. Zhang, C.E. Housecroft, J.A. Zampese, *Dalton Trans.* 39 (2010) 1941.
- [13] Stoe & Cie, X-Area, version 1.52: Program for the Acquisition and Analysis of Data; *Stoe & Cie GmbH*: Darmstadt, Germany, 2005.
- [14] R.H. Blessing, *Acta Cryst. A51* (1995) 33.
- [15] A.L. Spek, *Acta Cryst. D65* (2009) 148.
- [16] G.M. Sheldrick, *Acta Cryst. A64* (2008) 112.
- [17] H.H. Yaoy, W.T. Huangy, J.M. Loz, F.L. Liaox, P. Chattopadhyay, *J. Coord. Chem.* 58 (2005) 975.
- [18] H. Kargar, R. Kia, M.N. Tahir, Private Communication.
- [19] H. Kargar, R. Kia, H.K. Fun, A. Jamshidvand, *Acta Cryst. E65* (2009) m515.
- [20] H. Kargar, R. Kia, H.K. Fun, Private communication.
- [21] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* (1987) S1.
- [22] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Oxford: Pergamon Press, 1994.
- [23] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.